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Spectroscopic characterization of the oxo-transfer reaction from a bis(μ-oxo)dicopper(III) complex to triphenylphosphine†

Svetlana V. Pavlova,[a] Kelvin H.-C. Chen[a,b] and Sunney I. Chan*[a,b]

[a] *Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan. E-mail: chans@chem.sinica.edu.tw; Fax: +886-2-2783-1237; Tel: +886-2-2783-1237*

[b] *Department of Chemistry, National Tsing Hua University, Hsinchu, 300, Taiwan*

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The oxygen-atom transfer reaction from the bis(μ-oxo)dicopper(III) complex $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ **1**, where L = *N*,*N*,*N*′,*N*′ -tetraethylethylenediamine, to PPh_3 has been studied by UV-vis, EPR, ^{1}H NMR and Cu K-edge X-ray absorption spectroscopy in parallel at low temperatures (193 K) and above. Under aerobic conditions (excess dioxygen), **1** reacted with PPh_3, giving $O{=}PPh_3$ and a diamagnetic species that has been assigned to an oxo-bridged dicopper(II) complex on the basis of EPR and Cu K-edge X-ray absorption spectroscopic data. Isotope-labeling experiments ($^{18}O_2$) established that the oxygen atom incorporated into the triphenylphosphine oxide came from both complex **1** and exogenous dioxygen. Detailed kinetic studies revealed that the process is a third-order reaction; the rate law is first order in both complex **1** and triphenylphosphine, as well as in dioxygen. At temperatures above 233 K, reaction of **1** with PPh_3 was accompanied by ligand degradation, leading to oxidative N-dealkylation of one of the ethyl groups. By contrast, when the reaction was performed in the absence of excess dioxygen, negligible substrate (PPh_3) oxidation was observed. Instead, highly symmetrical copper complexes with a characteristic isotropic EPR signal at g = 2.11 were formed. These results are discussed in terms of parallel reaction channels that are activated under various conditions of temperature and dioxygen.

Introduction

Copper ions are found in the active sites of many redox-active metalloproteins involved in important biological electron and oxygen transfer reactions.[1–3] During recent years much effort has been directed toward modeling the reactions of copper enzymes with dioxygen in order to elucidate the mechanism of dioxygen activation by copper monooxygenases as well as to develop efficient catalytic systems for selective oxidation of organic substrates by dioxygen.[4–9] In this regard, the series of copper–dioxygen complexes, such as (μ-η^2:η^2-peroxo)dicopper(II) and bis(μ-oxo)dicopper(III), have been most extensively studied since these binuclear metal sites have been proposed as models of reactive intermediate(s) at the active sites of copper monooxygenases.[3–6,8–12] Understanding how synthetic model systems and copper proteins utilize dioxygen to oxidize substrates is a timely and important research topic.

Several examples of intermolecular oxygen-atom transfer reactions mediated by copper–dioxygen species with the Cu_2O_2 core are described in the literature.[13–20] Mahadevan *et al.*[14] have studied the oxidation of triphenylphosphine (PPh_3) with Cu_2O_2 complexes supported by *N*,*N*′-di-*tert*-butyl-*N*,*N*′-dimethyl-1,2-ethanediamine under conditions of slow equilibrium between the bis(μ-oxo) and side-on peroxo isomers in 2-methyltetrahydrofuran, and demonstrated that the (μ-η^2:η^2-peroxo)dicopper(II) appears to be the better oxygen-atom transfer reagent compared to its bis(μ-oxo)dicopper(III) counterpart. An exception was noted for the bis(μ-oxo) complex supported by *N*,*N*,*N*′,*N*′-tetramethylpropanediamine, which quantitatively converts PPh_3 into triphenylphosphine oxide ($O{=}PPh_3$).[13] These authors have suggested that accessibility of the substrate (PPh_3) to the Cu_2O_2 core is an important factor that governs the observed difference in reactivity.[14] Irrespective of whether the bis(μ-oxo) or side-on peroxo isomer, supported by peralkylated diamines ligands, mediates the oxygen-atom transfer directly, the oxidation of PPh_3 is facile under a dioxygen atmosphere.[13–15] In the case of the bis(μ-oxo)dicopper(III) species capped with the aromatic N-donor ligand Me_2tpa, the reaction with PPh_3 at 195 K under Ar causes the stoichiometric displacement of bound O_2, producing the $[Cu(Me_2tpa)(PPh_3)]^+$ complex.[17] By contrast, it was recently reported[18] that sulfoxidation reactions mediated by the bis(μ-oxo)dicopper(III) complex supported by the ligand L^{Py1Bz} proceeded under anaerobic conditions *via* a direct oxygen-atom transfer mechanism involving formation of a binary complex between the substrate and the metal oxo-species. Oxidation of the amine moiety of the supporting ligand to the corresponding *N*-oxide by (μ-η^2:η^2-peroxo)dicopper(II) complex has also been reported.[19] It was suggested that the oxo-transfer reaction here is effected by a very reactive intermediate derived from (μ-η^2:η^2-peroxo)dicopper(II) which was formed in the steady-state. Recently, the facile oxidation of a variety of exogenous substrates mediated by (μ-η^2:η^2-peroxo)dicopper(II) isomers with R–$MePY_2$ ligands has also been reported.[20]

We report here parallel EPR, ^{1}H NMR and Cu K-edge X-ray absorption spectroscopic and UV-vis kinetic studies of the chemistry between a bis(μ-oxo)dicopper(III) complex and PPh_3 under various conditions in order to derive more information on the process of oxygen-atom transfer from the bis$[Cu_2(\mu\text{-}O)_2]^{2+}$ core to exogenous substrates. Toward this end, we have deployed various spectroscopic methods to characterize the chemical species formed during the putative oxo-transfer reaction, and to elucidate the role of exogenous dioxygen. In addition, we have resorted to kinetic studies in order to elucidate the role of the various reactants in the overall reaction mechanistic scheme. Specifically, we have focused on the known complex,[21] $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ **1**, supported by *N*,*N*,*N*′,*N*′ -tetraethylethylenediamine (L), which is relatively stable at low temperatures, to probe the details of the reaction(s) with PPh_3.

Results and discussion

Preparation and spectroscopic characterization of $[Cu^{III}_2(\mu\text{-}O)_2(L)_2](X)_2$ (X = ClO_4^-, BF_4^-) (1)

Bis(μ-oxo)dicopper(III) complex **1**, was prepared *in situ* by treating $[LCu(MeCN)]BF_4$ or $[LCu(PhCN)]ClO_4$ with dioxygen

† Electronic supplementary information (ESI) available: Plots of the pseudo-first-order rate constant k_{obs} obtained from analysis of initial rates as a function of $[PPh_3]_0$ (Fig. S1) or $[O_2]_0$ (Fig. S2) for the reaction of **1** with PPh_3. Fig. S3: Kinetic traces of the absorbance change at 404 nm during the reaction of **1** with PPh_3 under dioxygen in the absence and presence of $O{=}PPh_3$. See http://www.rsc.org/suppdata/dt/b4/b406692h/

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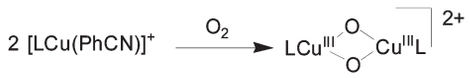
in anhydrous dichloromethane at 193 K, according to the published procedure[14] (Scheme 1). Spectroscopic characterization of **1** was performed in CH_2Cl_2 at 193 K. Optical absorption spectroscopy showed the characteristic intense LMCT bands at λ_{max} = 307 and 404 nm. EPR of a frozen solution of **1** was silent at 77 K. The Cu K-edge absorption spectrum of **1** exhibited a pre-edge feature at 8981.1 eV, corresponding to the 1s → 3d transition characteristic of Cu(III) compounds.[21] These spectroscopic data indicated that the oxygenated solution of the starting Cu(I) precursor is the bis(μ-oxo)dicopper(III) complex, in good agreement with the results reported previously by Stack *et al.*[21–23]



1

Scheme 1

In addition to the spectral data of **1** reported previously, we have monitored the formation of **1** by ^{1}H NMR spectroscopy at low temperature (193 K). The spectrum of $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ is quite simple. Chemical shifts for **1** at 1.40 ppm and 2.99–3.28 ppm are downfield shifted from the corresponding values in the case of the starting Cu(I) complex (see Experimental section). The lack of extensive broadening of the ^{1}H NMR resonances for the copper(III) species and the presence of relatively sharp peaks with chemical shifts in the normal region (0–10 ppm) is consistent with the diamagnetic behavior of **1**. Under slow oxygenation of a solution of the Cu(I) complex in CD_2Cl_2 at 193 K, we detected simultaneously resonances from the starting copper(I) precursor and the $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ species.

Reaction of $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ with PPh_3

The reactivity of **1** toward PPh_3 was examined under both limiting dioxygen (anaerobic) and excess dioxygen (aerobic) conditions at different temperatures. When the reaction was studied under aerobic conditions, excess dioxygen was simply added to the precursor Cu(I) complex during the formation of the bis(μ-oxo)dicopper(III) complex. For anaerobic conditions any excess O_2 remaining after the formation of the bis(μ-oxo)dicopper(III) complex was removed by bubbling Ar gas through the solution for 20 min at 193 K. The reaction with PPh_3 was followed for different reaction times as the experimental mixture was warmed in steps.

To a solution of complex **1** prepared as mentioned above, 2 equiv. of a precooled solution of PPh_3 in CH_2Cl_2 was introduced and aliquots of the experimental mixture were analyzed with time. This amount of PPh_3 was chosen so that only 50% would be converted to $O{=}PPh_3$ if only one of the bridging oxos in the Cu_2O_2 core of complex **1** was transferred to the PPh_3 during the oxo-transfer reaction and the reaction proceeded to completion. When the reaction was performed in the absence of excess dioxygen, negligible substrate (PPh_3) oxidation was observed. However, when the reaction was carried out under aerobic conditions, as can be seen in Fig. 1, at reaction time 5 min, 11% of the PPh_3 was already oxidized to $O{=}PPh_3$. The yield of $O{=}PPh_3$ increased slowly, reaching ~16.5% in 5 h and ~20% in 10 h at 193 K. Since the PPh_3 was in excess of the dicopper complex **1** in these experiments, these observations must clearly reflect the thermodynamics of the oxo-transfer reaction, namely

$$\mathbf{1} + PPh_3 \rightleftharpoons O{=}PPh_3 + \mathbf{2}$$

rather than the equilibrium between the bis(μ-oxo) and side-on peroxo isomers of **1**.

Both the extent of conversion of the PPh_3 to $O{=}PPh_3$ and the kinetics increased with temperature. The 20% conversion of PPh_3 to $O{=}PPh_3$ that took 10 h at 193 K could be attained within a reaction time of 15 min at 233 K. Slow warming of the experimental solution and keeping the sample at room temperature for one day yielded 43% conversion of the PPh_3 into $O{=}PPh_3$ (Table 1). The latter conversion was practically quantitative, if one took into consideration that there was a competing process of oxidative ligand N-dealkylation (*vide infra*) at the higher temperatures (≥233 K). Thus **1** was competent toward effecting an oxo-transfer reaction converting PPh_3 into $O{=}PPh_3$ under aerobic conditions. The process appeared to involve a stoichiometry of 1 : 1 with respect to **1** and PPh_3, or only one of the two oxo-ligands in the bis(μ-oxo)dicopper(III) complex. The experimental data obtained are comparable to those previously reported,[14] namely, the reactivity of **1** toward PPh_3 at 193 K lies between two closely related bis(μ-oxo)dicopper(III) complexes, one supported by *N*,*N*′-di-*tert*-butyl-*N*,*N*′-dimethyl-1,2-ethanediamine (50% yield of PPh_3O) and the other by *N*,*N*′-diisopropyl-*N*,*N*′-dimethyl-1,2-ethanediamine (~5% yield of PPh_3O). However, the authors quenched the reaction by adding ammonia to aliquots of the experimental mixture at room temperature. In contrast, in the present study, we demonstrated that warming of the reaction mixture to room temperature led to substantial enhancement of the reaction rate and almost complete oxygen-atom transfer.

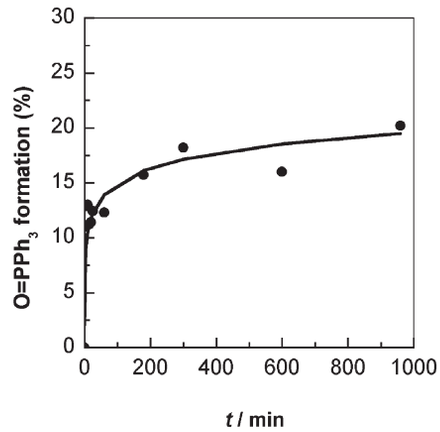


Fig. 1 Formation of $O{=}PPh_3$ calculated according to the stoichiometry of the reaction between **1** and PPh_3 in dichloromethane at 193 K under dioxygen as described by Scheme 3. $[\mathbf{1}]_0$ = 1.0 mM, $[PPh_3]_0$ = 2.0 mM, $[O_2]_0$ = 6.58 mM.

Kinetic studies

The reaction between bis(μ-oxo)dicopper(III) complex **1** and triphenylphosphine was followed spectrophotometrically by the intensity decrease of the characteristic absorbance at 404 nm due to the complex **1** in CH_2Cl_2 at 193 K. The reaction obeyed first-order kinetics in the presence of an excess amount of the PPh_3 under dioxygen conditions over the first 160 min (Fig. 2), and the rate constant was well described by the initial rate over the first 300 s (Fig. 2, inset). A plot of the pseudo-first-order rate constant k_{obs} against the initial concentration of triphenylphosphine under aerobic conditions provided a straight line: $y = 0.033x + (1 \times 10^{-6})$ ($R^2 = 0.9865$) with nearly zero intercept and a slope from which the pseudo-second-order rate constant $(3.3 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1} was obtained at the dioxygen concentration of 6.58 mM used (Fig. S1, ESI†).

When the reaction was carried out under Ar conditions, practically no change in absorbance was observed. Thus, the rate of the reaction was unequivocably established to be dioxygen concentration dependent. A plot of the initial reaction rates measured at a fixed PPh_3 concentration *vs.* the initial concentration of O_2 could be fitted to a straight line: $y = 0.013x + (6 \times 10^{-6})$ ($R^2 = 0.9856$) with essentially zero intercept and the pseudo-second-order rate constant $(1.3 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} was obtained at the PPh_3 concentration of 2.3 mM used (Fig. S2, ESI†). This result shows that the reaction is first order in dioxygen. In other words, dioxygen is serving as a catalyst in the oxo-transfer between complex **1** and PPh_3.

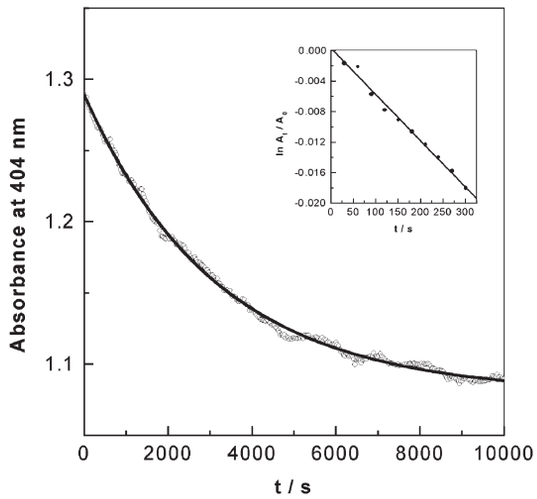


Fig. 2 A representative kinetic trace of the absorbance change at 404 nm during the reaction of **1** with excess PPh_3 in dichloromethane at 193 K under dioxygen. Experimental points superimposed by single-exponential fit: $[\mathbf{1}]_0$ = 0.053 mM, $[PPh_3]_0$ = 1.7 mM, $[O_2]_0$ = 6.58 mM. Inset: Plot of $\ln(A_t/A_0)$ *vs.* time based on the absorption change at 404 nm over the first 300 s and the corresponding linear fit.

To account for the experimental observations and to clarify the role of dioxygen, we have invoked the reaction mechanistic scheme shown in Scheme 2. We assume a rapid reaction between **1** and dioxygen to give an intermediate **1a**, followed by a slower oxo-transfer from **1a** to PPh_3 to give the product $O{=}PPh_3$ under the excess PPh_3 and dioxygen concentrations used in these experiments. In other words, we assume that the oxo-transfer reaction is preceded by the formation of a dioxygen adduct of the bis(μ-oxo)dicopper(III) complex **1**. The dioxygen that is invoked as the catalyst in step (a) is regenerated in step (b). Finally, since we are recording the kinetics at early times (initial rates), the slow step is assumed to be irreversible.

Scheme 2

Although no detectable intermediate was observed during the course of the kinetic measurements, we assume that **1a** was just present in the reaction mixture in miniscule amounts, and it was being consumed essentially as it is produced. Applying the steady-state assumption to the concentration of **1a** yielded the following rate law for the overall reaction (eqn. (1)):

$$\text{Rate} = -\text{d}[\mathbf{1}]/\text{d}t = \frac{k_1 k_2[\mathbf{1}][O_2][PPh_3]}{k_{-1} + k_2[PPh_3]} \quad (1)$$

From this result, it is clear that pseudo-first-order conditions would be obtained with the dioxygen concentration fixed at $[O_2]_0$, and when the kinetics was followed with the system flooded with respective to PPh_3 and set at $[PPh_3]_0$; that is,

$$\text{Rate} = k_{obs}[\mathbf{1}] \quad (2)$$

where

$$k_{obs} = \frac{k_1 k_2[PPh_3]_0[O_2]_0}{k_{-1} + k_2[PPh_3]_0} \quad (3)$$

Moreover, when step (b) is sufficiently slow compared with step (a) in the kinetic scheme to allow a pre-equilibrium to be established in step (a), $k_2[PPh_3]_0 \ll k_{-1}$, and

$$k_{obs} = \frac{k_1 k_2[PPh_3]_0[O_2]_0}{k_{-1}} \quad (4)$$

or

$$k_{obs} = Kk_2[PPh_3]_0[O_2]_0 = k_2'[PPh_3]_0[O_2]_0 \quad (5)$$

where $K = k_1/k_{-1}$ and $k_2' = k_2K$.

Thus, under pseudo-first order conditions, k_{obs} should be a linear function of $[PPh_3]_0$ under fixed aerobic conditions. Similarly, under fixed $[PPh_3]_0$, k_{obs} should increase linearly with increasing $[O_2]_0$. Since earlier we determined experimentally that $k_2'[O_2]_0 = (3.3 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1} and $k_2'[PPh_3]_0 = (1.3 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1}, the two sets of experiments yielded k_2' values that agreed within the experimental error of ~10%.

$$k_2' = \frac{k_{obs}}{[O_2]_0} = \frac{(3.3 \pm 0.3) \times 10^{-2}\,M^{-1}\,s^{-1}}{6.58 \times 10^{-3}\,M} = 5.0 \pm 0.4\ M^{-2}\ s^{-1}$$
$$k_2' = \frac{k_{obs}}{[PPh_3]_0} = \frac{(1.3 \pm 0.1) \times 10^{-2}\,M^{-1}\,s^{-1}}{2.3 \times 10^{-3}\,M} = 5.6 \pm 0.4\ M^{-2}\ s^{-1} \quad (6)$$

EPR and Cu K-edge absorption spectroscopy

In order to monitor any changes in the Cu oxidation state during the reaction with PPh_3, aliquots of the experimental mixtures were taken at 193 K at different reaction times and subjected to EPR and Cu K-edge X-ray absorption spectroscopy. The experimental solutions examined at different reaction times were EPR silent, that is, no paramagnetic species were formed in significant quantities over the course of the reaction, or only diamagnetic species were involved.

The solutions, studied by EPR, were also examined by Cu K-edge X-ray absorption spectroscopy. Reaction of **1** with PPh_3 under aerobic conditions resulted in the spectral changes shown in Fig. 3. Most significantly, the spectrum of **1** exhibited a pre-edge feature, centered at 8981.1 eV, corresponding to the 1s → 3d transition of Cu(III),[21] and also specific transitions at 8986.7 and 8993.2 eV, which could be assigned, respectively, as the 1s → 4p + LMCT shakedown and 1s → 4p transitions.[21,23] These features were more easily discerned in second derivative spectra (Fig. 4), where the positions of the peaks became more prominent against the background. As a result of the chemistry between **1** and PPh_3 the intensity of the 1s → 3d transition decreased, and a pre-edge feature at 8978.2, corresponding to Cu(II),[23] appeared. In addition, a shift to lower energy (~0.4 eV) to 8986.3 eV was also observed for the 1s → 4p + LMCT shake-down and (~0.6 eV) to 8992.6 eV for the 1s → 4p transitions. When the reaction was carried out under excess of dioxygen

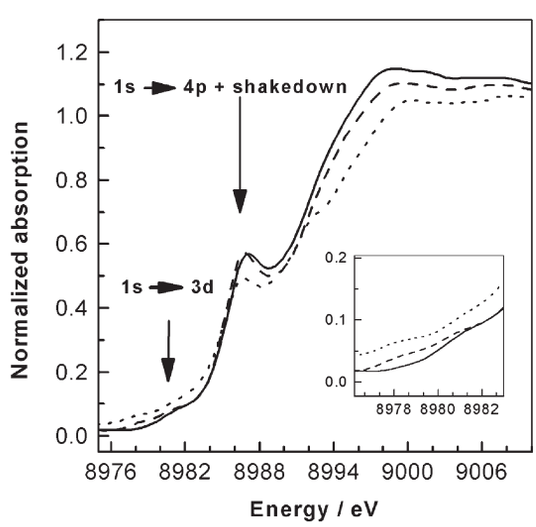


Fig. 3 Cu K-edge X-ray absorption recorded at 77 K for **1** (solid line), and after the reaction of **1** with PPh_3 under excess dioxygen for 30 min (dashed line) and 4 h (dotted line) in CH_2Cl_2 at 193 K. Inset: Pre-edge region amplified.

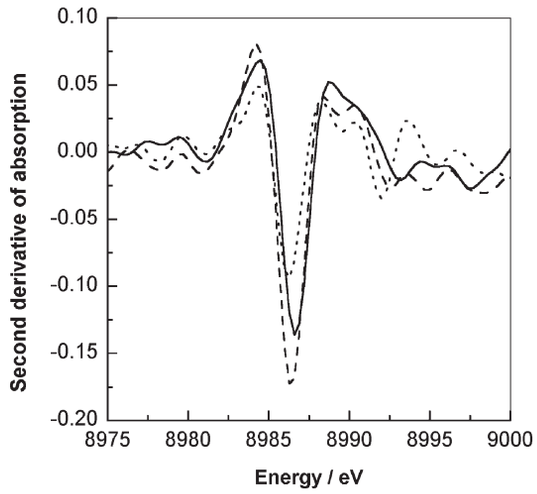
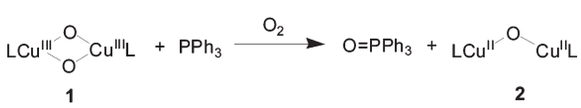


Fig. 4 Second-derivative of the Cu K-edge absorption recorded at 77 K for **1** (solid line); and after the reaction of **1** with PPh_3 under excess dioxygen for 30 min (dashed line) and for 4 h (dotted line) in CH_2Cl_2 at 193 K.

for more then 4 h, there was further increase in the intensity of the features at 8978.2 eV and at 8992.0 eV, which are typically observed for tetragonal Cu(II) complexes.[24]

Taking into account that the reaction between complex **1** and PPh_3 occurs principally in the presence of dioxygen and diamagnetic copper(II) species are formed, these observations are consistent with the reaction scheme highlighted in Scheme 2. First, the overall oxo-atom transfer from the bis(μ-oxo)dicopper(III) core of **1** to PPh_3 is 1 : 1. However, an essential feature of the oxo-atom transfer chemistry is that the reaction is catalyzed by dioxygen. The kinetics suggest that the dioxygen forms an adduct with complex **1**, and it is this adduct that mediates the transfer of one of the bridging oxo atoms in the bis(μ-oxo)dicopper(III) complex to PPh_3 to form $O{=}PPh_3$. Had both oxo atoms of the bis(μ-oxo)dicopper(III) core of **1** been transferred to PPh_3 molecules, then the original Cu(I) precursor would be regenerated. In this scenario, the overall chemistry would then be described by the reaction $2PPh_3 + O_2 \rightarrow 2O{=}PPh_3$, with the Cu(I) precursor serving as the catalyst. Finally, **1** is reduced to the diamagnetic complex **2**, in accordance with Scheme 3.



1 **2**

Scheme 3

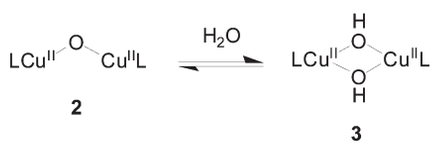
However, contrary to expectation, the reaction does not proceed to completion at 193 K, despite the strong acidity of the PPh_3. Presumably, the μ-oxo in the bis(μ-oxo)dicopper(III) core is sufficiently stable that the overall equilibrium (Scheme 2) remains very much to the left at 193 K. As the temperature is increased, the position of the equilibrium Scheme 2 is gradually shifted, until at room temperature the reaction is essentially complete (Table 1). We have established that such an equilibrium is indeed in effect by following the reaction to longer times (kinetics no longer fit exponential behavior after several hours) as well as observing the effects of exogenously added products on the overall kinetics. The addition of $O{=}PPh_3$ to our reaction mixtures has been found to accelerate the approach of the system toward chemical equilibrium (Fig. S3, ESI†).

The oxo-bridged dicopper(II) complex

As a consequence of the chemistry highlighted in Schemes 2 and 3, the oxidation state of the copper centers in the bis(μ-oxo)dicopper(III) complex would change from +3 to +2, as confirmed by X-ray absorption edge results. Many examples of (μ-oxo)dicopper(II) complexes are known.[25–31] Most of them demonstrate antiferromagnetic properties and their frozen solutions are EPR silent at 77 K.[27,29] But only a few of these (μ-oxo)dicopper(II) compounds have been isolated,[25,27,29] because of their instability and strong nucleophilic properties. In polar solvents, like methanol, (μ-oxo)dicopper(II) species disproportionate to mononuclear Cu(II) complexes.[28,29] In the presence of small amounts of water, these complexes are also known to transform into the bis(μ-hydroxo)dicopper(II) species **3**,[28–31] (Scheme 4).

Table 1 Conversion of PPh_3 into $O{=}PPh_3$ (%) for the reaction time 15 min in CH_2Cl_2

Temperature/K	Aerobic condition	Anaerobic condition
193	11.0	3
203	14.2	—
213	14.7	—
223	16.5	—
233	17.8	—
Further, slow warming to room temperature.	42.8	10



2 **3**

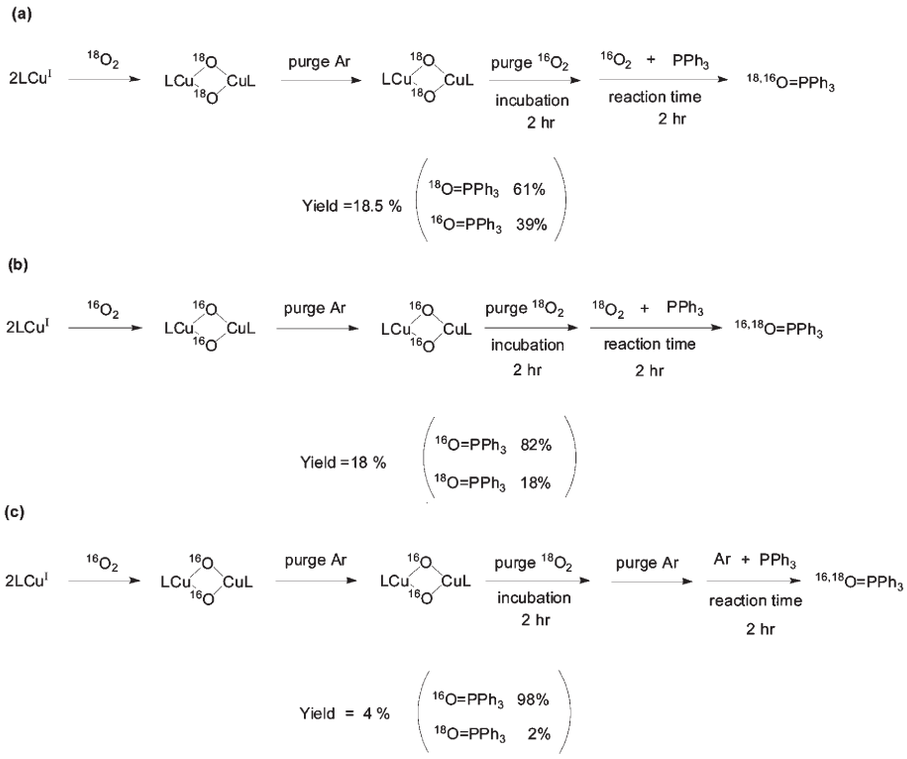
Scheme 4

Our attempts to isolate (μ-oxo)dicopper(II) complex **2** resulted in separation of the bis(μ-hydroxo)dicopper(II) compound **3**, which we have characterized by X-ray crystallography. The structural characteristics of the obtained complex were analogous to those previously reported.[32] Complex **3** crystallized in the $P2_1/c$ monoclinic system. The coordination geometry around copper atom is slightly distorted from planarity, consisting of the N_2O_2 donor set defined by the two bridging OH groups and the two nitrogens from the bidentate ligands. The IR spectrum of this compound included sharp bands at 3518 and 3423 cm^{-1}, which corresponded to the O–H stretching vibrations from the bridging hydroxo groups and from lattice water, respectively. Complex **3** is EPR silent (77 K), and exhibited a broad d–d absorption at λ = 560 nm (ε 260 M^{-1} cm^{-1}) and an intense feature at λ = 361 nm (ε 1500 M^{-1} cm^{-1}). The latter could be ascribed to a $OH^- \rightarrow$ Cu(II) LMCT transition, as found for other bis(μ-hydroxo)dicopper(II) complexes.[30,31,33] The perchlorate anion was not coordinated to the metal, but there are hydrogen bond interactions between one of the oxygens of the perchlorate group and the bridging hydroxide group.

Finally, Kitajima *et al.*[27,29] and Karlin *et al.*[28] reported the facile oxidation of PPh_3 by the related (μ-oxo)dicopper(II) species under ambient temperature with replacement of the oxygen atom in the (μ-oxo)dicopper(II) species by PPh_3 molecule and the generation of Cu(I)–PPh_3 complexes. However, no Cu(I) complexes were observed in the reaction of **1** with PPh_3 in the present study. Thus, we have obtained no evidence for the reaction $\mathbf{1} + 4PPh_3 \rightarrow 2O{=}PPh_3 + 2LCu(I)–PPh_3$.

Isotope-labeling experiments

In order to verify the role of the exogenous dioxygen in the reaction of **1** with PPh_3 and in an attempt to probe the nature of the dioxygen adduct formed with the bis(μ-oxo)dicopper(III), namely **1a**, we have performed a series of isotope-labeling experiments, where either $^{16}O_2$ and/or $^{18}O_2$ was used in the preparation of **1**, and the final outcome of the bridging oxo in **1** was queried in the product $O{=}PPh_3$ in the presence of the dioxygen bearing the other isotopomer. The results of these experiments are schematically presented in Scheme 5(a, b, c).

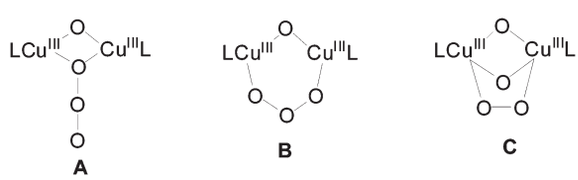


Scheme 5

These isotope-labeling experiments clearly demonstrated that the oxygen atom transferred to the PPh_3 came both from the bis(μ-oxo)dicopper(III) complex and the exogenous dioxygen, as expected for a process that was catalyzed by the dioxygen *via* the formation of an "active species". In other words, there was scrambling of the oxygen isotopes from **1** and the dioxygen either during the formation of **1a** or during the oxo-transfer reaction from **1a** to PPh_3. However, the data did suggest that the oxo atom transferred to the PPh_3 came primarily from the bis(μ-oxo)dicopper(III) complex, and there was only partial scrambling of the oxygen atoms between the μ-oxos in the bis(μ-oxo)dicopper(III) complex and the dioxygen in the adduct. Moreover, it was clear from the results obtained for (c) in Scheme 5 that the direct exchange between the oxygen pools between the bis(μ-oxo)dicopper(III) complex and the exogenous dioxygen was too slow to affect the outcome of the isotope labeling experiments. In this control experiment, we observed only 2% of the exogenous dioxygen ($^{18}O_2$) in the product ($O=PPh_3$) after a prolonged equilibration between complex **1**, that had previously been labeled with $^{16}O_2$, with the exogenous dioxygen $^{18}O_2$, followed by purging with Ar and re-equilibration with fresh Ar and PPh_3. Under these conditions, the oxo-transfer was presumably non-catalytic, so that the rate was very slow and only a small quantity of $O=PPh_3$ was produced by direct reaction of the PPh_3 with the bridging oxos in the bis(μ-oxo)dicopper(III) complex. Thus, the scrambling of the oxygen isotopes in these experiments did not occur during the formation of **1a**, but rather during the oxo-transfer reaction from **1a** to PPh_3.

Mechanistic considerations

The results of the $^{16}O_2/^{18}O_2$ isotope labeling experiments are consistent with the reaction scheme proposed in Scheme 2. But at this stage we can only speculate upon the nature of the "reactive species" **1a**, which are undetectable under experimental conditions. One possibility is that **1a** is a (μ-oxo)(μ(1,1)-ozonide)dicopper(III) complex, namely, dioxygen has merely added to one of the bridging μ-oxos in **1** to form an "oxonide" adduct (structure **A** in Scheme 6). Such an adduct should be relatively labile, which would account for the rapid pre-equilibrium given by step (a) in Scheme 2. More importantly, the ozonide formation is expected to activate the remaining



Scheme 6 Possible structures of adduct **1a**.

μ-oxo in the adduct, rendering it more facile for oxo-atom transfer to PPh_3 to form $O=PPh_3$. This scenario would fit well with the limiting $^{16}O_2/^{18}O_2$ isotope scrambling results. At this juncture, we could not rule out other structures for the adduct **1a**, for example, structures **B** and **C** in Scheme 6, although structure **B** is expected to lead to greater $^{16}O_2/^{18}O_2$ isotope scrambling than observed experimentally.

It is conceivable that the exogenous dioxygen somehow promotes the formation of the side-on peroxo isomer by shifting the equilibrium between the bis(μ-oxo) and side-on peroxo forms. It has been shown[14,15,20] that the peroxo-isomer is a better oxygen-atom transfer reagent, so that under rapid interconversion between the two isomers,[14,33] the oxo-transfer from complex **1** to PPh_3 could be facilitated. Although this hypothesis is quite attractive, under our experimental conditions, we have observed in the UV-vis spectra solely the absorbance from the bis(μ-oxo)dicopper(III) isomer and a small shoulder at 360 nm (corresponding to the bis(μ-hydroxo)dicopper(II) species), which appeared after the reaction of **1** with PPh_3.

Stoichiometric formation of copper(II) clusters of higher nuclearity

As noted earlier, when the formation of the bis(μ-oxo)dicopper(III) complex and the reaction between **1** and PPh_3 was carried out in dry CH_2Cl_2 under large excess of dioxygen, the diamagnetic species **2** was produced (Scheme 3). No EPR signal was observed for these reaction mixtures. However, when the formation of the bis(μ-oxo)dicopper(III) complex was carried out under limiting dioxygen (less than stoichiometric to form the 2:1 $Cu:O_2$ complex totally), a strong isotropic signal with *g* value centered at 2.11 was observed in the EPR spectrum (Fig. 5). Under these conditions, the excess Cu(I) starting precursor in the solution could provide a source of

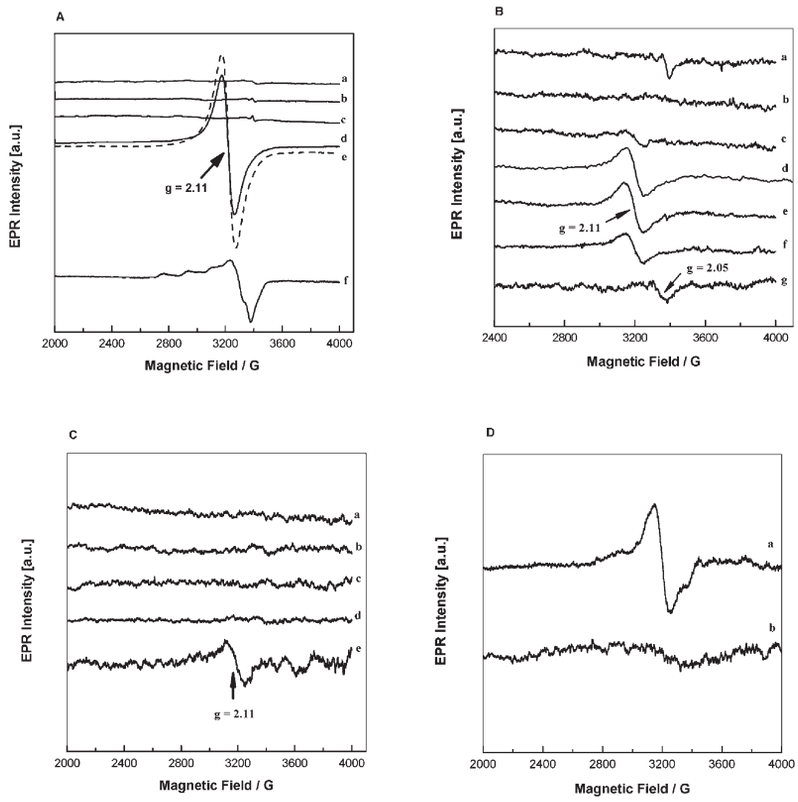


Fig. 5 EPR spectra (77 K) recorded during the reaction of **1** with PPh_3 in CH_2Cl_2 at 193 K (A) Reaction followed under Ar (anaerobic conditions): (a) Spectrum of an initial solution of **1** (4.3 mM) without PPh_3; (b)–(e) spectra recorded after reaction with PPh_3 for 10 min (b), 1 h 30 min (c), 4 h (d), ~12 h (e), and further warming to room temperature and work up with methanol (f). (B) Reaction followed under Ar (anaerobic conditions) using a sample of partially reduced **1** prepared by incomplete oxidation of the starting Cu(I) complex. (a) Spectrum of an initial solution of **1** (0.65 mM) without PPh_3; (b)–(g) spectra recorded after reaction with PPh_3 for 10 min (b), 20 min (c), 1 h (d), 2 h (e), 9 h (f) and further warming solution to room temperature with exposure to air (g). (C) Reaction followed under Ar (anaerobic conditions) using a sample of partially reduced **1** in the presence of ½ equiv. of the Cu(I) precursor. (a) Spectrum of an initial solution of complex **1** (0.65 mM); (b) spectrum obtained after introduction of ½ equiv. of Cu(I) complex into the solution of **1**; and (c)–(e) spectra obtained after reaction with PPh_3 for 15 min (c), 1 h (d), and ~12 h (e). (D) Reaction of **1** with PPh_3 followed under Ar (anaerobic condition) for reaction time ~12 h (a); and further warming to room temperature (b).

reducing equivalents to partially reduce some of the bis(μ-oxo)dicopper(III) complex already formed to give the mixed valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ core.

The experimental conditions that led to the formation of this new copper species are as follows: After incomplete oxygenation of a sufficiently concentrated solution (8.7 mM) of the Cu(I) starting material, and the addition of 2 equivalents of PPh_3, the experimental mixture was left stirring at 193 K under anaerobic conditions (1 atmosphere of argon). Initially, we detected practically no EPR spectra (Fig. 5(A)(a)–(c)). Then, at a reaction time of ~3–4 h, an isotropic signal was detected (Fig. 5(A)(d),(e)). The latter EPR signal is typical of Cu(II) complexes with octahedral symmetry,[34] but is also found for symmetrical triangular copper(II) cluster complexes with equivalent g_x, g_y, g_z values.[35–37]

The new copper species with the isotropic EPR signal was formed only when there was insufficient dioxygen in the sample to oxidize all the starting Cu(I) complex to the bis(μ-oxo)dicopper(III) complex, and when the subsequent oxo-transfer reaction to PPh_3 was performed under Ar conditions. Despite the fact that the PPh_3 was incubated with incompletely oxidized **1** under anaerobic conditions, relative facile oxidation of PPh_3 to $O{=}PPh_3$ was observed in these experiments (*vide infra*). Typically, under anaerobic conditions, practically no oxo-atom transfer from **1** to PPh_3 was observed.

In order to highlight these features, we summarize the results of several independent experiments in Fig. 5 and Table 2:

(1) As can be seen from Fig. 5(B)(a), under conditions of incomplete oxidation of the starting Cu(I) complex at 193 K, we could register a weak EPR signal. This weak EPR spectrum most likely originated from the Cu(II) in the reoxidized starting material. It is possible that there was also a contribution from the mixed-valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ species that was expected to be formed after reduction of the bis(μ-oxo)dicopper(III) complex by the excess starting Cu(I) precursor. Upon purging the sample with Ar and the introduction of PPh_3, the EPR spectrum of the sample became silent. However, with time, a broadened isotropic signal with the characteristic $g = 2.11$ grew in gradually (Fig. 5(B)(c)–(f)), as was observed before (Fig. 5(A)(d),(e)). Further warming of this sample to room temperature and exposure to dioxygen, resulted in a blue solution with a weak type 2 Cu(II) EPR at $g \sim 2.05$ (Fig. 5(B)(g)). This experiment highlighted the requirement for excess reducing equivalents in the solution to give the copper species with the isotropic EPR signal as well as the relatively facile oxygen atom transfer from the mixed-valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ species to PPh_3 at 193 K in Ar in this experiment.

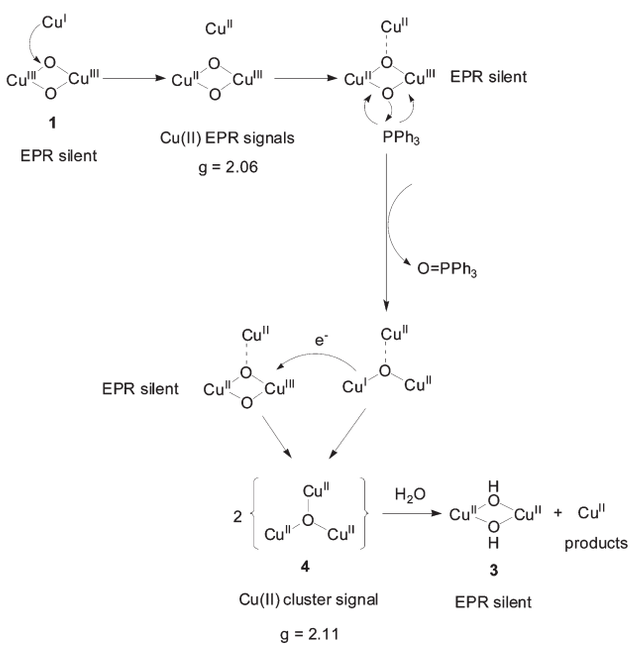
(2) In a second set of experiments, we added 1/2 equivalent of the Cu(I) starting material to a solution containing 0.65 mM of the preformed bis(μ-oxo)dicopper(III) species (total copper 1.95 mM) at 193 K. No EPR signal was observed initially upon the introduction of PPh_3 (under Ar). The broadened isotropic signal was detected after a reaction time of ~12 h. These spectral changes in the EPR pointed unequivocally to the generation of a new Cu(II) cluster species, whose concentration depended on the concentration of bis(μ-oxo)dicopper(III) species as well as on the concentration of reducing equivalents available to partially reduce the preformed bis(μ-oxo)dicopper(III) complex. When the concentration of the mixed valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ species was higher as in the first set of experiments (Fig. 5(A)), the isotropic EPR signal was much more intense than in the present experiment (Fig. 5B, C(e), D(a)).

Although the structural details remained unclear, on the basis of the experimental observations summarized above, it is possible to propose the following scenario for the formation of the putative trinuclear copper cluster species. When there

Table 2 Summary of experiments on $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ samples containing residual (due to incomplete oxidation) or added $[LCu(PhCN)]^+$ precursor: Evidence for enhanced reactivity of $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ species towards oxo-transfer to PPh_3

Details on the preparation of the sample	Reaction time at 193 K/min	EPR signal (*g*-value)	Conditions
Experiment 1			
Initial concentration of $[LCu(PhCN)]^+$ = 8.7 mM; complete formation of **1** (4.3 mM)	10–720	Silent	Aerobic
Experiment 2			
Initial concentration of $[LCu(PhCN)]^+$ = 8.7 mM; incomplete formation of **1** (<4.3 mM)	10–120 240 720	Silent Isotropic (2.1) Isotropic (2.1)	Anaerobic
Experiment 3			
Initial concentration of $[LCu(PhCN)]^+$ = 4.0 mM; incomplete formation of **1** (<2.0 mM)	720	Weak isotropic (2.1)	Anaerobic
Experiment 4			
Initial concentration of $[LCu(PhCN)]^+$ = 1.3 mM; complete formation of **1** (0.65 mM)	—	Silent	Anaerobic
Initial concentration of $[LCu(PhCN)]^+$ = 1.3 mM; complete formation of **1** (0.65 mM); additional Cu(I) precursor (0.35 mM) subsequently added	15–60 720	Silent Isotropic (2.1)	
Experiment 5			
Initial concentration of $[LCu(PhCN)]^+$ = 1.3 mM; incomplete formation of **1** (<0.65 mM); no additional Cu(I) precursor added	— 10 20–540	Weak Silent Isotropic (2.1)	Anaerobic

was excess of reduced Cu(I) starting material in the sample during the preparation of the bis(μ-oxo)dicopper(III) complex, or when there was insufficient dioxygen to transform all the starting material to the bis(μ-oxo)dicopper(III) species, a mixed-valence copper(II,III)–dioxygen active species could be formed (Scheme 7). When this mixed-valence species further reacted with PPh_3 under anaerobic conditions (under Ar), and there was a second mixed-valence complex to receive the extra electron from the product copper species remaining after the oxo-transfer reaction to PPh_3, two trinuclear copper(II) clusters **4** would result (Scheme 7). Presumably it is this trinuclear copper(II) species that is the origin of the broad isotropic EPR signal at $g \sim 2.11$.



Scheme 7 Proposed scheme for the oxo-transfer reaction from partially reduced **1** to PPh_3 and the formation of trinuclear copper(II) clusters under dioxygen limiting conditions.

Analysis of aliquots of the experimental mixture, examined at low temperatures, as well as integration of EPR spectra, showed that the percent of conversion of PPh_3 into $O{=}PPh_3$ correlated well with the amount of trinuclear Cu(II) clusters formed, consistent with the chemistry proposed in Scheme 7. For example, in the first set of experiments (Fig. 5(A)), where we started with a Cu(I) concentration of 8.7 mM, ~1.98 mM was converted to Cu(II), according to the intensity of the EPR signal at $g = 2.11$, after a 4 h incubation at 193 K, corresponding to ~22% conversion to Cu(II) based on the initial Cu(I) concentration. The observed conversion of PPh_3 into $O{=}PPh_3$, based on quantitation of GC data, was consistent, with ~15.4% conversion of the starting Cu(I) to Cu(II). After a reaction time of 16 h, 44% of the Cu(I) was converted to Cu(II) based on the formation of $O{=}PPh_3$ as detected by GC; and the Cu(II) concentration was ~3.4 mM, which corresponded to the oxidation of 39% of the starting Cu(I) to Cu(II). For comparison, when the oxo-atom transfer reaction was performed under excess dioxygen at 193 K, the conversion of PPh_3 into $O{=}PPh_3$ was about 16%, after a reaction time of 5 h. However, the solution was EPR silent indicating that only diamagnetic copper species were involved in the chemistry.

The oxo-transfer chemistry from the mixed-valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ to PPh_3 is expected to be facile, as compared to the corresponding process from the bis(μ-oxo)dicopper(III) complex, which has proven to be relatively inert. Earlier, we had already commented on the stability of the μ-oxo in the bis(μ-oxo)dicopper(III) core at 193 K in consideration of the thermodynamics of the oxo-atom transfer from the bis(μ-oxo)dicopper(III) complex to PPh_3. The corresponding oxo-atom transfer from the mixed-valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ complex should be more favorable thermodynamically, as we have just demonstrated here. In other words, one electron titration of the bis(μ-oxo)dicopper(III) core promotes oxo transfer from the cluster to PPh_3 at 193 K. Chan *et al.*[38] has hypothesized such a mixed-valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ unit as an actual active oxygen intermediate in the alkane hydroxylation chemistry mediated by pMMO. More recently, it has also been demonstrated that the disproportionation of bis(μ-oxo)dicopper(III) complex may afford a reactive intermediate such as (μ-oxo)(μ-oxyl radical)dicopper(III) species, which may participate in the C–H bond activation of external substrates.[39]

Unfortunately, our attempts to isolate the Cu(II) cluster complex was unsuccessful. Warming the resulting experimental mixture afforded a blue–green solution with a green precipitate. After separation and re-dissolving of the green precipitate in methanol, we obtained an EPR spectrum that is typical of Cu(II) ions in a quasi-square planar coordination environment[34,40] (Fig. 5A(f)).

NMR spectroscopy studies

^1H NMR was also used to monitor the reaction between **1** and PPh_3 under both aerobic and anaerobic conditions. Addition of

PPh_3 to a dichloromethane-d_2 solution of **1** under excess oxygen at 193 K resulted in a decrease in the intensity of the resonances assigned to the bis(μ-oxo)dicopper(III) complex (Fig. 6(A)) without any noticeable changes in the chemical shifts and linewidths of these signals.

An apparent equilibrium was reached after several hours, without further decrease in the intensity of the signals. Upon slow warming of the experimental mixture to ambient temperatures, however, the resonances of **1** completely disappeared, in part due to the formation of the species **2**, but also to the thermal decomposition of the $[Cu^{III}_2(\mu\text{-}O)_2]^{2+}$ core. New signals appeared, centered at δ 2.83 (d) and 1.08 (t) ppm corresponding to the ligand's protons of the newly formed diamagnetic species **2** (Fig. 6(A)). It was possible to observe these signals at 233 K, because the rate of reaction between **1** and PPh_3 had increased sufficiently relative to that at 193 K, with the concomitant increase in the concentration of the (μ-oxo)dicopper(II) species. The lack of any line broadening in these signals was consistent with the formation of a diamagnetic species **2**, in accordance with Scheme 3.

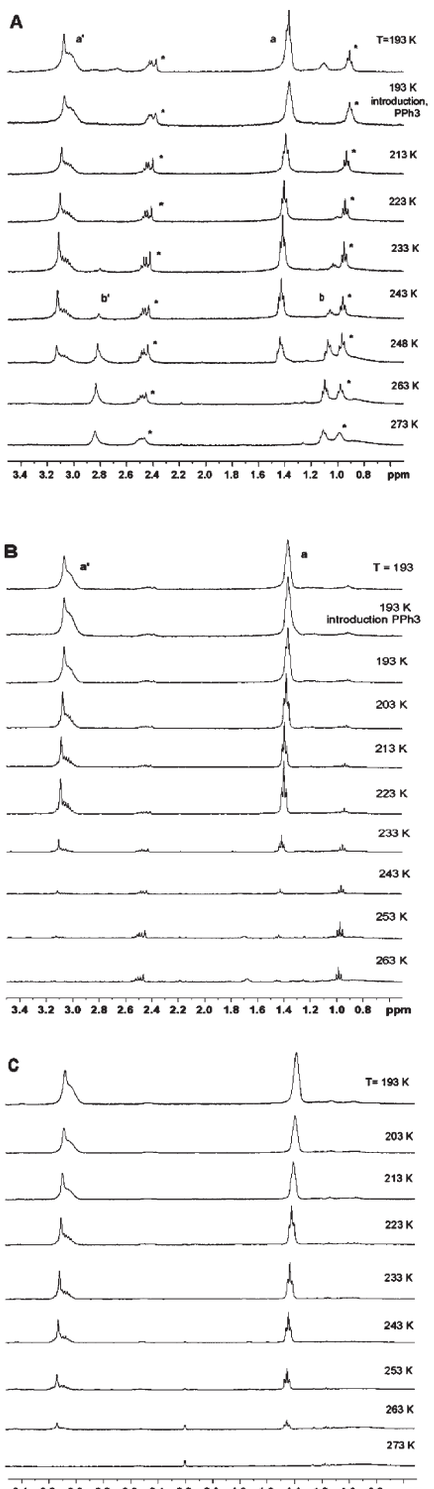
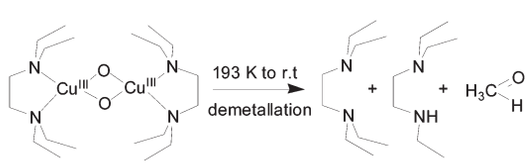


Fig. 6 Changes in the ^{1}H NMR spectra (CD_2Cl_2) observed upon introduction of PPh_3 into the solution of **1** under dioxygen conditions (A) and under anaerobic conditions (Ar) (B) followed by warming the reaction mixture to ambient temperature. (a, a′) denote the resonances from the $-CH_3$ and $-CH_2-$ protons, respectively, of complex **1**; resonances (b, b′) are assigned to the $-CH_3$ and $-CH_2-$ protons of new species **2**. (C) Decomposition of **1**. Spectral range: 0.5–3.5 ppm.

In contrast, when a dichloromethane solution of PPh_3 was added to **1** under anaerobic conditions, the intensity of the bis(μ-oxo)dicopper(III) complex remained practically unchanged. In addition, no signals were observed at δ 2.83 and 1.08 ppm, even though some oxo-transfer from **1** to PPh_3 had taken place under these conditions (10% converted to $O{=}PPh_3$; see Table 1) upon warming the experimental solution to room temperature (Fig. 6(B)). The changes in the ^{1}H NMR spectra observed upon warming the experimental mixture containing **1** and PPh_3 under Ar conditions were the same as that noted upon the decomposition of **1** (Fig. 6(C)). These observations are consistent with our earlier conclusion that the oxo-transfer reaction between the $[Cu^{III}_2(\mu\text{-}O)_2(L)_2]^{2+}$ complex and PPh_3 occurs principally in the presence of dioxygen, providing additional support for O_2 as a catalyst for the oxygen-atom transfer reaction from **1** to PPh_3, as we have already demonstrated in the kinetic studies described earlier.

Decomposition of bis(μ-oxo)dicopper(III) complex

Reaction of **1** with PPh_3 was accompanied by the process of complex degradation, involving oxidative ligand sidearm N-dealkylation at sufficiently high temperatures. This process apparently proceeded through the monooxygenase reaction[33] (Scheme 8) similar to that reported previously by Tolman *et al.*[33,41–43] Basically, N-dealkylation began at temperatures above 233 K, since no products of complex degradation were found at temperature ≤233 K for reaction times as long as 10 h. After work up, a mixture of intact ligand *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (L) and *N*,*N*,*N*′-triethylethylenediamine (L′), the product of N-dealkylation with the loss of one ethyl group, were identified by GC/GC-MS analysis. When the decomposition of the **1** was followed under anaerobic conditions, the molar ratio of L : L′ was found to be 3 : 1, in accordance with Scheme 8. However, when the sample was incubated with PPh_3 under aerobic conditions for 2 h and then gradually warmed to room temperature over a 3 h period, L : L′ increased to 6 : 1, as expected because of the competing oxo-atom transfer to PPh_3 at the lower temperatures. Acetaldehyde was identified as a co-product by GC, and ^{1}H NMR spectroscopy at 2.18 ppm (Fig. 6(C)).



Scheme 8 Decomposition of $[Cu^{III}(\mu\text{-}O)_2(L)_2]^{2+}$.

Interestingly, N-dealkylation chemistry did not occur in the presence of 10% of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). According to GC analysis, the decomposed solution contained the intact ligand *N*,*N*,*N*′,*N*′-tetraethylethylenediamine and the TEMPO oxidation product 2,2,6,6-tetramethyl-1-piperidine. Since TEMPO is well established as a Lewis base in d-block coordination chemistry and can bind to Cu(II) with the formation of $CuCl_2$(TEMPO) and $CuBr_2$(TEMPO) adducts,[44] introduction of TEMPO into the solution of **1** may lead to association of the nitroxide radical to one of copper(III) atoms,

and cause redistribution of the electron density in the Cu_2O_2 core and suppress the process of ligand N-dealkylation.

Summary

In this study, we have followed the oxygen-atom transfer from **1** to PPh_3 at 193 K and above. The reactivity of **1** toward PPh_3, as well as the details of the oxo-transfer chemistry was found to be strongly dependent on the experimental conditions.

The bis(μ-oxo)dicopper(III) complex was found to be surprisingly inert when an attempt was made to carry out the oxygen-atom transfer under anaerobic conditions in Ar. If the reaction was carried out under excess of dioxygen, it produced $O{=}PPh_3$ and a diamagnetic oxo-bridged dicopper(II) species **2** or the bis(μ-hydroxo)dicopper(II) species **3**. Isotope-labeling experiments established that the oxygen atom incorporated into the $O{=}PPh_3$ came either from the bis(μ-oxo)dicopper(III) complex or from the exogenous dioxygen. The major labeled $O{=}PPh_3$ product contains the oxygen isotope derived from **1**.

The reaction was shown to be catalytic, with O_2 as the catalyst. However, it was stoichiometric with respect to the starting copper bis(μ-oxo)dicopper(III) complex. Depending on the temperature, the reaction was complete when equilibrium had been reached with respect to the product $O{=}PPh_3$, or when the bis(μ-oxo)dicopper(III) complex was completely transformed to the bis(μ-hydroxo)dicopper(II) compound. At 193 K the reaction was slow and the equilibrium remained toward the reactant side, but as the temperature was increased, complete oxygen-atom transfer was observed.

The relative inertness of the bis(μ-oxo)dicopper(III) complex toward PPh_3 under anaerobic conditions could be alleviated by reductive activation of the bis(μ-oxo)dicopper(III) core to give the mixed valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ core. This reductive activation could be accomplished by preparing the bis(μ-oxo)dicopper(III) complex in the presence of excess Cu(I) starting precursor. The latter provided a source of reducing equivalents to convert the bis(μ-oxo)dicopper(III) core in the complex to the more reactive mixed valence $[Cu^{II}Cu^{III}(\mu\text{-}O)_2]^+$ core. Under these conditions, the PPh_3 oxidation proceeded in a facile manner and resulted in the formation a highly symmetrical Cu(II) compound, presumably the triangular copper(II) cluster complex, with its characteristic isotropic copper EPR signal. Recently, Taki *et al.* reported that a mixed-valence bis(μ-oxo) trinuclear copper(II,II,III) species could be assessed by the reaction of the copper(I) starting material with the bis(μ-oxo)dicopper(III) complex.[45] Earlier, the structure of the mixed-valence trinuclear copper(II,II,III) complex, was reported by Cole *et al.*[46]

At higher temperatures near ambient conditions, ligand degradation competed with the oxo-transfer reaction, and the PPh_3 oxidation was accompanied by ligand side arm N-dealkylation of one of the ethyl groups.

The results of the present study extended the earlier work of Mahadevan and others,[13,14] by providing greater insight into the intimate mechanistic details of the chemistry of the system. This advance was only possible by a detailed kinetic study of the system to ascertain the reaction mechanism, and by appealing to a number of physical methods, including X-ray absorption spectroscopy, UV-visible spectroscopy, EPR, NMR, and isotope labeling, to identify or rationalize the products as well as some of the intermediates formed during the time course of the reaction.

Experimental

General procedures

All chemical except the complexes, were obtained from commercial sources as a reagent grade quality and used as received unless noted otherwise. Acetonitrile (Merck, HPLC grade) and benzonitrile (Merk) used in the syntheses of the copper(I) complexes were distilled from P_4O_{10} (Merck). *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (L) was purchased from Aldrich (98%) and distilled *in vacuo* from NaH before use. Purity of the ligand (99.9%) was controlled by GC analysis. Triphenylphosphine (Aldrich) and triphenylphosphine oxide (Merk) were purified and dried according to published procedures.[47] Dichloromethane (Aldrich, 99.8%, not stabilized) was stirred over concentrated H_2SO_4, washed with de-ionized water, followed by Na_2CO_3 (satd.) solution and again water, dried under anhydrous $MgSO_4$ and finally distilled from P_4O_{10} in the absence of light. For kinetics studies, dichloromethane (Merck, spectroscopy grade, 99.9%, stabilized with 2-methyl-2-butene) was freshly distilled from CaH_2. Diethyl ether (Mallinckrodt) was distilled from Na/benzophenone. Oxygen gas (99.8%, Fong Ming), used for oxygenation, was dried by passing it through two short columns in succession of P_4O_{10} and Drierite, followed by a cold trap (193 K). $^{18}O_2$ (95–98% atom ^{18}O) was obtained from Cambridge Isotope Laboratories Inc. and used without further purification. The extent of incorporation of ^{18}O into the products of the oxidation reaction was accomplished by GC-MS analysis. The air/moisture-sensitive materials were prepared and handled either in a Braun Company inert-atmosphere glove box under N_2, where the samples for IR, NMR and UV-vis spectroscopy were also prepared, or by using standard Schlenk and vacuum line techniques. The solvent and solutions were deoxygenated either by three freeze–thaw vacuum/purge cycles with argon or by bubbling argon (20 min) directly through the solutions. Saturated solutions of O_2 and Ar in CH_2Cl_2 were prepared by bubbling the gas through the liquid for 20 min at room temperature and 30 min at low temperature. The solubility of O_2 in dichloromethane was accepted to be 5.8 mM at 293 K according to the literature.[48,49] The changes in the reagent concentrations as well as dioxygen concentration in dilute dichloromethane with the change in temperature were calculated by using equations: $d_T = 1.370(2) - 0.00180(2)T$ (T in °C) and $C_T = C_{20\,°C}\ (d_T/d_{20\,°C})$.[49] Consequently the concentration of O_2 in the saturated solution of dichloromethane at 193 K was calculated as 6.58 mM.

Methods

GC analysis was performed on a Hewlett-Packard 6890 series gas chromatograph, equipped with capillary injector and flame ionization detector using a 50-m HP-1 capillary column. GC-MS analysis was performed on Hewlett-Packard 6890 series gas chromatograph equipped with capillary injector and flame ionization detector, using a 60-m HP-5 capillary column interfaced with mass selected detector (MS) (HP5972). Infrared spectra were measured in a Nujol mull on a Perkin-Elmer 283 instrument. ^1H NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 and/or a mixture of CD_2Cl_2–CH_2Cl_2. (1 : 10) on a Bruker AMX-400 spectrometer. Chemical shifts (in ppm) are referenced either to an internal standard of Me_4Si, or to the residual solvent peak (dichloromethane) whose chemical shift was referred to Me_4Si in the low-temperature experiments.

EPR spectroscopy

EPR spectra were recorded on a Bruker E-500 spectrometer, equipped with Bruker TE102 cavity. In the EPR experiments, sample temperature was maintained at 77 K by using a liquid-nitrogen finger Dewar. The EPR samples were prepared by rapid transferring, through a cannula, the chilled experimental mixture (193 K) from the reaction flask to the EPR tube, equipped with a septum port, and immediately frozen in liquid nitrogen. The copper spin concentration was measured against copper perchlorate standard solutions (7200, 1440, 288, 58 μM) in MeOH–CH_2Cl_2 (1 : 5, v/v). The EPR spectra of these copper standards were recorded at 77 K with microwave power 5 mW. Upon performing baseline corrections, the spectra were double integrated from 2500 to 3500 G, and a standard curve, correlating the EPR intensity with copper concentration, was generated. The copper spin concentration measured for the various samples against the copper perchlorate standards were then inferred

from the EPR signal intensity and the standard curve. The same samples, used in the EPR spin quantitation experiments, were subsequently analyzed by gas chromatography.

X-Ray absorption spectroscopy

X-Ray absorption spectroscopy data were collected at the National Synchrotron Radiation Research Center, (NSRRC) (beam line Wiggler 17C, Si (111) double crystal monochromator, 1.5 GeV, internal energy calibration) in Hsinchu (Taiwan). All samples for X-ray absorption spectroscopy experiments were loaded into a sample holder (1.4 cm × 1.4 cm × 0.2 cm) covered with sheets of Kapton. The samples were prepared by rapidly transferring, through a cannula (with application of a slight positive pressure of oxygen/argon), the cold experimental mixture (193 K) from the reaction flask to the sample holder, equipped with a septum port, and then rapidly frozen in liquid nitrogen. Samples were stored under liquid N_2 until ready for use. During the measurements, the samples were kept at 77 K (liquid nitrogen). Fluorescence data were measured using an Ar-filled ionization chamber detector equipped with a Ni filter and Soller slits. Data represented an average of 10–16 scans. Data reduction included energy calibration assigning the first inflection point of the Cu foil to 8980.3 eV, pre-edge subtraction using a polynomial function, spline removal, and normalization. Spectra were recorded at two different run times and two separate preparations of **1** with and without PPh_3.

Kinetic measurements

Time-resolved low-temperature absorption spectra were obtained by using a Hewlett-Packard 8453 diode array spectrometer equipped with custom-designed immersion fiber-optic quartz probe with 10 mm path length (Hellma, Inc.), fitted to the Schlenk vessel (50 cm^3) with stopcock and vacuum inlet. The Schlenk vessel with experimental solution and with immersion fiber-optic probe was placed in a Dewar filled with acetone. To maintain and control low temperature, a copper-tubing coil was inserted into the acetone-filled Dewar through which cold methanol was circulated from an external source (Neslab cryocool system: CC-100 II Immersion Cooler, Agitainer, and Cryocontrol Temperature Controller). The temperature in the Dewar was controlled by an ACE Glass Model 8292 organic-liquid filled thermometer (−100 to 50 °C). The temperature variation was within ±1 °C.

The kinetics of the reaction between **1** and PPh_3 were studied in dichloromethane at 193 K by following the time dependence of the absorbance at 404 nm due to **1**. A starting solution of complex **1** was prepared *in situ* by the reaction of $[LCu(MeCN)]BF_4$ precursor and dry oxygen gas (see preparation) in the reaction vessel equipped with the fiber-optic quartz probe and a stir bar. Typically a small volume of concentrated dichloromethane solution of $[LCu(MeCN)]BF_4$ was injected into 40–50 cm^3 of the dry, deoxygenated dichloromethane (placed in the reaction flask), followed by bubbling precooled oxygen gas through this solution for 20 min to accomplish the formation of the bis(μ-oxo)dicopper(III) complex at 193 K. The concentration of $[LCu(MeCN)]BF_4$ precursor used in the kinetic experiments was in the range 0.8–1.1 mM. Before the $[LCu(MeCN)]BF_4$ was transferred into the flask with the UV-Vis probe, a background scan with pure solvent was taken. After formation of the bis(μ-oxo)dicopper(III) complex, a small volume (0.5 cm^3) of concentrated solution of the triphenylphosphine in CH_2Cl_2 was introduced by a cannula, and the rate of the reaction was then followed.

For anaerobic conditions O_2 was removed by gently bubbling Ar gas into the solution of the **1** for 30 min. During the bubbling of Ar gas no spectral change of the bis(μ-oxo)dicopper(III) complex was observed at this temperature. To vary the concentration of dioxygen in the reaction of **1** with PPh_3, calibrated volumes of dichloromethane, saturated with Ar or O_2, were added to the previously degassed solution of bis(μ-oxo)dicopper(III) complex by using Hamilton air-tight syringes. Each kinetic run was repeated three times. The relative standard errors of the single k_{obs} was ~5% and for the average values ~10%. The analysis of the raw kinetic data was performed by using Origin 6.0 Professional Microcal Software.

Preparations

$[Cu(PhCN)_4]ClO_4$ and $[Cu(MeCN)_4]BF_4$ were prepared according to literature methods.[50,51] The complexes $[LCu(PhCN)]ClO_4$ and $[LCu(MeCN)]BF_4$ were prepared as described previously.[14] Equimolar amounts of $[Cu(PhCN)_4]ClO_4$ or $[Cu(MeCN)_4]BF_4$ and *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (L) were combined in CH_2Cl_2 in a volumetric flask in the dry box to yield colorless solutions of $[LCu(PhCN)]ClO_4$ or $[LCu(MeCN)]BF_4$, respectively, of known concentrations that were varied over the range 0.08–8.7 mM. $[LCu(PhCN)]ClO_4$: ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.29 (12H, t, 4 CH_3), 2.73 (4H, s, 2 CH_2), 2.82 (8H, q, 4 CH_2), 7.5 (m, C_6H_5), 7.7 (m, C_6H_5). ^{1}H NMR (CD_2Cl_2, 193 K): δ 1.19 (12H, s, 4 CH_3), 2.7–2.9 (12H, m, 6 CH_2). 7.6 (m, C_6H_5), 7.7 (m, C_6H_5). The solutions of Cu(I) precursor were prepared freshly as needed and used immediately.

CAUTION: Perchlorate salts of the metal complexes with organic ligands are potentially explosive and should be handled with care and in small quantities.

$[Cu^{III}_2(\mu\text{-}O)_2(L)_2](X)_2$ (X = ClO_4^-, BF_4^-) (1). Bis(μ-oxo)-dicopper(III) complex **1** was generated *in situ* as described previously[14] by the reaction of $[LCu(PhCN)]ClO_4$ or $[LCu(MeCN)]BF_4$ precursor and dry oxygen in highly purified dry CH_2Cl_2 by bubbling O_2 gas through the solution for ~5–20 min with stirring. The concentrations of Cu(I) precursor used were in the range 0.08–8.7 mM. The initially colorless solution became yellow–brown or deep brown depending on the concentration of the starting Cu(I) complex. Spectroscopic characterizations of **1** were performed in CH_2Cl_2 at 193 K. EPR (9.517 GHz, 77 K): silent; UV-Vis, λ_{max}/nm (ε/M^{-1} cm^{-1}): 307 (17000), 404 (24000). Cu K-edge spectrum (4.3 mM, 77 K) revealed a transition at 8981.1 ± 0.5 eV (data from three separate preparations). ^{1}H NMR (CD_2Cl_2): δ 1.4 (12H, t, 4 CH_3), 2.99–3.28 (12H, m, 6 CH_2).

$[Cu^{II}_2(\mu\text{-}OH)_2(L)_2](ClO_4)_2\cdot H_2O$ (3). A yellow–brown solution of **1** (1 mM) in CH_2Cl_2 at 193 K was prepared as described above (0.10 g, 0.174 mmol of $[Cu(PhCN)_4]ClO_4$ precursor). When the solution of **1** in CH_2Cl_2 was allowed to warm to room temperature, a blue solution resulted. Addition of an equal volume of the Et_2O yielded a blue precipitate, which was recrystallized from CH_2Cl_2–Et_2O (1 : 3), washed with Et_2O and vacuum-dried (0.037 g, 59%). Anal. Calc. for $C_{20}H_{52}Cl_2Cu_2N_4O_{11}$: C, 33.24; H, 7.2; N, 7.75%. Found: C, 33.39; H, 7.37; N, 7.53%. IR (Nujol), ν_{max}/cm^{-1}: 3518 (μ-OH), 3423 (H_2O), 1088 (ClO_4^-), 627 (ClO_4^-). UV-Vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}): 560 (260), 361 (1500).

Reaction of $[Cu^{III}_2(\mu\text{-}O)_2(L)_2](ClO_4)_2$ with PPh_3

The starting complex $[LCu(PhCN)]ClO_4$ was prepared by combining $[Cu(PhCN)_4]ClO_4$ (34 mg, 0.06 mmol) and *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (0.01279 cm^3, 0.06 mmol) in CH_2Cl_2 (25 cm^3) in the glove box. A solution of **1** was generated from $[LCu(PhCN)]ClO_4$ (0.06 mmol) and excess dioxygen as mentioned above. Then, 2 equiv. (with respect to complex **1**) of precooled solution of PPh_3 (15.7 mg, 0.06 mmol) in CH_2Cl_2 (2 cm^3) was introduced by cannulation and the mixture was stirred at 193 K. To monitor the products of the reaction with time at 193 K, aliquots were taken using a cannula, quenched at low temperature with 7 M ammonia in CH_3OH, then 32% ammonia, followed by repetitive extraction with CH_2Cl_2. The combined organic layers were dried over

$MgSO_4$, filtrated and were subjected to GC/GC-MS analysis. The conversion of PPh_3 into $O{=}PPh_3$ was calculated on the basis of the signals area in the GC chromatograms ($O{=}PPh_3$/PPh_3) by using the internal standard method. *trans*-Stilbene oxide was used as the internal standard. Mass recovery of the products was ≥90%. GC data were obtained using the following conditions: [150 °C (1 min) at 40 °C min^{-1} to 250 °C (10 min)], t_R/min, PPh_3: 8.36; $O{=}PPh_3$: 11. GC-MS data were obtained under conditions: [150 °C (1 min) at 20 °C min^{-1} to 250 °C (16 min)], t_R/min, (*m*/*z*), PPh_3: 13.2 (262, M^+); $O{=}PPh_3$: 21.7 (278, M^+); $^{18}O{=}PPh_3$: 21.7 (280, M^+).

Oxidative N-dealkylation reaction

Ligand isolation. A solution (25 cm^3) of bis(μ-oxo)-dicopper(III) complex **1** (0.03 mmol) was prepared as described above. 2 equivalents of PPh_3 (0.06 mmol) in CH_2Cl_2 (2 cm^3) were added and the mixture was stirred at 193 K for 2 h. For anaerobic conditions, excess O_2 was removed by gently bubbling Ar through the solution for 15 min at 193 K. When this solution was allowed to slowly warm and incubate for overnight at room temperature under positive dioxygen, or argon pressure, respectively, a blue or green solution was obtained. A solution (10 cm^3) of concentrated (30%) ammonia was added and the mixture was stirred vigorously giving blue aqueous and light yellow CH_2Cl_2 layers. The aqueous layer was separated and further extracted with CH_2Cl_2 (3 × 5 cm^3). The combined organic layers were dried over $MgSO_4$ and solvent was removed in *vacuo* giving an oily yellow mixture of products (L and L′). These products were subsequently characterized by GC/GC-MS and ^1H NMR spectroscopy and compared with authentic compounds. ^1H NMR ($CDCl_3$), L′: δ 1.01 (6H, t, 2 CH_3), 1.11 (3H, t, CH_3), 2.49–2.57 (6H, m, 3 CH_2), 2.63–2.68 (4H, m, 2 CH_2); L: δ 1.04 (12H, t, 4 CH_3), 2.49–2.52 (12H, m, 6 CH_2). GC, t_R/min, L′: 8.42; L: 9.52 under conditions: [70 °C (1 min) at 20 C° min^{-1} to 200 °C (10 min)]. GC-MS, t_R/min (*m*/*z*), L′: 22.2 (144, M^+), L: 24.96 (172, M^+) under conditions: [33 °C (5 min) at 6 °C min^{-1} to 200 °C (5 min)].

Identification of acetaldehyde from the decomposition of $[Cu^{III}_2(\mu\text{-}O)_2(L)_2](ClO_4)_2$. A small amount (0.5 cm^3) of the blue solution resulting from the decomposition of complex **1** under anaerobic conditions was removed from the reaction vessel and was passed through a short column with neutral activated alumina. The column was washed with CH_2Cl_2 (2 × 1 cm^3). Copper compounds were retained on the column while the organic products eluted. Acetaldehyde was identified from the resultant solution by GC-MS analysis by comparison of its mass spectra and retention time to an authentic sample. GC-MS, t_R/min (*m*/*z*): 4.55 (44, M^+), at conditions [32 °C (7 min) at 10 °C min^{-1} to 200 °C (5 min)].

Crystal structure determination of $[Cu^{II}_2(\mu\text{-}OH)_2(L)_2](ClO_4)_2$

Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromatized Mo-Kα radiation (λ = 0.7107 Å). Unit cell parameters were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Intensity data collected by use of ω–2θ scan mode. All intensity data were collected for Lorentz polarization and absorption (empirical ψ corrections).

Crystal data. $C_{20}H_{50}Cl_2Cu_2N_4O_{10}$, M = 704.62, monoclinic, space group $P2_1/c$ (no. 14), a = 7.6177(10), b = 17.850(3), c = 13.9471(17) Å, β = 122.147(12)°, U = 1605.7(4) $Å^3$, T = 298(2) K, Z = 2, μ(Mo-Kα) = 1.542 mm^{-1}, 3036 reflection measured, 2814 unique (R_{int} = 0.0220) which were used in all calculations. The final $wR(F^2)$ was 0.1084 (all data).

CCDC reference number 245728.

See http://www.rsc.org/suppdata/dt/b4/b406692h/ for crystallographic data in CIF or other electronic format.

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